

The Theory of Gasification and its Application
to Graphite and Metallurgical Coke

by W. Peters and G.-W. Lask

Bergbau-Forschung GmbH, Essen-Kray

The theory of heterogeneous reactions^{1,2)} is applicable to the combustion and gasification of solid fuels. In connection herewith the passage of materials, i.e. the diffusion of the reacting gas through the boundary film and its penetration into the pores of the fuel, plays an important part, in dependency upon the temperature. A great number of measured values agree fairly well with the theoretical postulates.

For the determination of the reactivity, which varies in dependency upon the coking conditions, one preferred measuring method is prevailing today 3). The relation between the measured results and the coking conditions on the one side(4) and the suitability of the coke for metallurgical purposes on the other side(5) has been the object of a recent publication.

1. Theoretical bases of the Kinetics of the heterogeneous reactions in the gasification of coke

1.1. The rapidity constant of the chemical reaction

The gasification of fixed carbon with carbon dioxide (Boudouard's reaction) is a reaction of the first order(6). Thus, the speed of the reaction



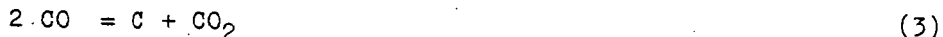
is governed by the equation:

$$\frac{dx}{dt} = k \cdot 0 \cdot m \cdot c \quad (2)$$

where

- x = quantity of converted carbon (g)
- t = reaction time (sec)
- m = quantity of coke (g)
- O = sum of the external and internal surfaces ($\frac{\text{cm}^2}{\text{g}}$)
- c = concentration of CO_2 ($\frac{\text{g}}{\text{cm}^3}$)
- k = reaction speed constant ($\frac{\text{cm}^3}{\text{cm}^2 \text{ sec}}$)

In the range of the technically interesting temperatures the back reaction, i.e. the decomposition of the carbon monoxide



does not play any part.

Equation (2) indicates the effective conversion in such cases where k is so small that the stream of gas can reach the reactive surface quickly enough. At sufficiently low temperatures this will always be the case; For Boudouard's reaction on industrial coke the upper temperature limit is situated at about 1100 °C.

When the reaction gas flows through a bed of coke (Fig. 1), formation of CO leads to a continuous decrease in the CO_2 concentration. Moreover, the speed of flow will increase, which is due to the increase of the number of molecules engaged in Boudouard's reaction. In these conditions, the quantity of CO_2 converted in the unit of time along a layer of infinitely small thickness is determined by the equation

$$\frac{dn}{dt} = k \cdot 0 \cdot \frac{m}{l} \cdot c(x) \cdot dx = -d[v(x) \cdot c(x)] \quad (4)$$

where n = C atoms transferred
 m = quantity of coke (g)
 l = height of the layer (cm)
 $c(x)$ = CO_2 concentration at point x (g/cm³)
 $v(x)$ = voluminal velocity at point x (cm³/sec)

Let us assume that the stream of CO_2 having a speed v_0 and a concentration c_0 penetrates into a coke layer of equal cross sectional area at any point; then the speed v_0 at any point of this layer is

$$v(x) = \frac{2v_0 \cdot c_0}{c_0 + c(x)} \quad (5)$$

Substitution of equation (5) into equation (4) and integration over x from zero to 1 leads to

$$2v_0 \cdot c_0 \int_{c_0}^{c_1} \frac{1}{c(x)} \cdot d\left[\frac{c(x)}{c_0 + c(x)}\right] = - \int_0^1 k \cdot 0 \cdot \frac{m}{l} dx \quad (6)$$

After integration between the limits indicated equation (6) adopts the following form:

$$2 \ln \frac{2c_1/c_0}{1 + c_1/c_0} + \frac{1 - c_1/c_0}{1 + c_1/c_0} = - \frac{k \cdot 0 \cdot m}{v_0} \quad (7)$$

where c_1 = the concentration of CO_2 in the outgoing gas (g/cm³)

Often the differentiation plays a great part in the experimental determination of the reaction speed. m , c_0 and v_0 can be fixed in such a way that the required apparatuses do not become too expensive. c_1 can be determined by gas analysis; its value should range between 40 and 80 %. With lower CO_2 concentrations we come into a range where the concentration of CO inhibits Boudouard's reaction (10-13). Higher CO_2 concentration, by contrast, require a very high accuracy of analysis, as in

their range even great changes of the reaction speed entail only slight modifications of the CO_2 concentration.

With the experimental conditions as described and the values of CO_2 concentration found in the outgoing gas, the product $k \cdot O$ can be calculated quite simply. As, however, it is difficult to determine the surface of reaction O , k and O are combined to form the reaction speed constant k_m which is based upon the weight unit instead of the unit of surface:

$$k_m = k \cdot O \quad (8)$$

This value k_m is called "reactivity" in the following chapters; its dimension is $\text{cm}^3/\text{g sec}$.

If the method used for the determination of the reactivity involves direct weighing of the loss of weight of the coal, whilst the CO_2 concentration in the outgoing gas, c_1 , differs only slightly from its concentration c_0 when entering the reaction chamber, it is easier to use equation (2) in the form:

$$\frac{dx}{dt} = k' \cdot m \cdot c' \quad (9)$$

where k' = reaction speed constant ($1/\text{sec}$)
 c' = concentration of CO_2 (g/cm^3) under the existing conditions
 concentration of CO_2 (g/cm^3) under standard conditions

In this case the loss of weight during gasification is indicated by k' , and the following numerical relation exists between k_m and k' :

$$k' = 5,02 \cdot 10^{-4} k_m \quad (10)$$

1.2. Reactivity as a function of temperature

The dependence of the reactivity upon temperature is expressed in Arrhenius's formula:

$$k_m = H \cdot e^{-\frac{E}{RT}} \quad (11)$$

where H = the frequency factor ($\text{cm}^3/\text{g sec}$)
 E = activation energy ($\text{kcal}/\text{Mol.}$)
 R = gas constant ($\text{kcal}/\text{mol degree}$)
 T = the absolute temperature (degrees Kelvin)

By plotting $\log k_m$ or $\log k'$ against $\frac{1}{T}$, we obtain a straight line with the gradient $-\frac{E}{R}$. From this gradient, the activation energy E can be de-

terminated. Figure 2 shows schematically the run of this straight line within range I.

1.3. The influence of diffusion upon the reaction speed constant and the energy of activation.

The validity of all the foregoing considerations is unrestricted only as long as the problems of molecular passage of materials during the gasification process do not yet come into play. With rising temperatures, however, the chemical reactivity will increase to such a degree that the diffusion of the gasifying agent in the carbon and towards the carbon, as the slowest step of a whole chain of physical and chemical reactions, becomes the dominant factor (1,2).

1.4. Pore diffusion

With rising temperature the reaction speed increases in conformity with equation

$$k = k_0 \cdot e^{-\frac{E}{RT}} \quad (12)$$

and the diffusion speed according to equation:

$$D = D_0 \cdot T^{1,8} \quad (13)$$

where D = diffusion speed (cm^2/sec)
 D_0 = diffusion speed constant (cm^2/sec)

As k rises much more sharply than D , the concentration of the gasifying agent in the pores of the fuel begins to decrease, beyond a certain temperature limit, as compared with its concentration in the ambient gas. This means that the conversion can utilize the internal surface only to a lesser degree, as expressed in equation

$$\frac{dx}{dt} = \left(\frac{dx}{dt} \right)_{\max} \cdot \eta \quad (14)$$

Beyond a zone of transition the utilization coefficient η is proportional to the reciprocal value of the catalyser coefficient ρ (1,2).

$$\rho = L \cdot \sqrt{\frac{2k}{rD}} = \frac{1}{\eta} \quad (15)$$

where L = length of pores (cm)
 r = diameter of pores (cm)

For coke it is admissible to replace the length of pores by half the diameter of the lump $d/2$. Substitution of equations (14) and (15) into equation (2) leads to

$$\frac{1}{m} \frac{dx}{dt} = 0. c_0 \frac{1}{d} \sqrt{2 r D k} \quad (16)$$

As, according to equations (12) and (13), the reaction speed k rises much more rapidly than the diffusion speed D with the temperature,

$$\frac{dx}{dt} \approx e^{-\frac{E/2}{RT}} \quad (17)$$

This is to say that in the case of pore diffusion the activation energy is reduced to half its value. In figure 2 this is schematically represented by the straight line within range II.

1.5. Boundary film diffusion

If the reaction speed continues to increase with rising temperature, the conversion is restricted to the external surface of the fuel. Around the piece of coke forms a boundary film through which the gasifying agent will diffuse towards the place of the reaction. Under these conditions the reaction speed mainly depends on this diffusion process which is governed by Fick's first law:

$$\frac{dx}{dt} = - D F \frac{dc}{d\delta} \quad (18)$$

where F = external surface of the coke (cm^2)
 δ = distance from the coke surface (cm)

In the boundary layer the concentration shows a linear decrease:

$$\frac{dc}{d\delta} = - \frac{c_0}{\delta} ; \quad c = \frac{c_0}{\delta} \delta \quad (19)$$

Substitution into equation (18) leads to

$$\frac{dx}{dt} = D \cdot F \cdot \frac{c_0}{\delta} \quad (20)$$

The determination of δ is an aerodynamic problem which can be solved as follows: The transfer of heat on surfaces is governed by the general law:

$$\frac{dq}{dt} = \alpha \cdot F \cdot \Delta T \quad (21)$$

where q = quantity of heat (cal)
 α = coefficient of heat transfer ($\text{cal}/\text{cm}^2 \text{ sec}^\circ\text{C}$)

On the other side the flow of heat in a layer can be expressed as follows:

$$\frac{dq}{dt} = \lambda \cdot F \cdot \frac{dT}{d\delta} \quad (22)$$

where λ = thermal conductivity (cal/cm sec °C)

According to equation (19), the temperature gradient $\frac{dT}{d\delta}$ is constant

as well as $\frac{dc}{d\delta}$; thus,

$$\frac{dq}{dt} = \lambda \cdot F \cdot \frac{\Delta T}{\delta} \quad (23)$$

Division of equation (23) by equation (21) leads to the next equation from which the thickness of the boundary layer δ can be determined.

$$1 = \frac{\lambda}{\alpha} \delta ; \quad \delta = \frac{\lambda}{\alpha} \quad (24)$$

From many measurements the ratio $\frac{\alpha}{\lambda}$ is known for pieces of coke in a

free stream of gas, as well as for coke grains in layers and fluidized beds; as a rule the following basis is assumed:

$$Nu = b \cdot Re^a \quad (25)$$

where Nu = Nusselt's number

$$\left(\frac{\alpha \cdot d}{\lambda} \right)$$

Re = Reynolds number

$$\left(\frac{w \cdot d}{\nu} \right)$$

d = coke diameter

a and b = constants which are independent of the conditions of flow (cm/sec)

ν = kinematic viscosity

By substituting into equation (24) the value of $\frac{\alpha}{\lambda}$ obtained from equation (25), we get the thickness of the boundary layer δ whose value is substituted into equation (20):

$$\frac{dx}{dt} = D \cdot F \cdot \frac{b \cdot c_0}{d} \cdot Re^a \quad (26)$$

With sufficient accuracy the kinematic viscosity ν can be assumed to be equal to the diffusion speed D , whose dependency upon the temperature is expressed by equation (13). Using a shape factor f , the external sur-

244.

face of the mass of coke (m) can be calculated from the equation

$$F = \frac{6 f m}{\rho d} \quad (27)$$

where F = shape factor
 ρ = apparent density of the piece of coke (g/cm^3)

To derive c_o from the standard concentration c_{No} , the temperature T and the pressure p have to be taken into account as usually:

$$c_o = c_{No} \frac{273 p}{T 760} \quad (28)$$

Taking into account equations (13), (27) and (28) we obtain from equation (26) the final formula:

$$\frac{1}{m} \frac{dx}{dt} = 2.16 f b D_o^{1-a} \frac{c_N^p}{\rho} d^{a+2} T^{0.8 - 1.8a} \quad (29)$$

In practice, the power a is about 0.5, so that the final formula in most cases reads as follows:

$$\frac{1}{m} \frac{dx}{dt} = 2.16 f b \sqrt{D_o} \frac{c_N^p}{\rho} \frac{1}{d \sqrt{d}} \frac{1}{T^{0.1}} \quad (30)$$

In the range of boundary film diffusion the dependency upon the temperature T is almost negligible, as appears from the horizontal stretch of the curve in range III (see fig. 2). The proportionality to $1/d^{1.5}$ reflects the great importance of the piece size in gasification processes at very high temperatures.

1.6. Dependency on the conditions of gasification

Practically, each range of reaction is characterized by a straight line in the Arrhenius diagram, the three straight sections being linked together by shorter or wider arches. If the conditions are changed, the straight lines are shifted, as will be shown in detail in the light of the three final equations, applicable to the three ranges, viz. (2), (19), and (30).

In the range of chemical reaction the particle size d is not influential upon the intensity of gasification. In the other ranges crushing of the coke leads to a higher intensity of gasification; in fact, in range II the way of diffusion up to the internal surface is reduced, whereas in range III the reactive external surface is enlarged. In the Arrhenius diagram (Fig. 3) the straight lines show a parallel upward displacement with decreasing particle size in the range II and III, whereas the transition zone between range I and II is shifted to the left, i.e. towards higher temperatures.

In ranges I and II the increase in the internal surface O entails a proportional intensification of gasification. In range II, where CO_2 is completely converted on the external surface, the internal surface does not play any part. In the Arrhenius diagram (Fig. 4) the straight lines show a parallel upward displacement with increasing surface O in ranges I and II, and the transition from range II to III is shifted to the right.

The speed is influential upon the decrease in CO_2 concentration during the passage through the layer of coke. Only for this reason, not directly the intensity of gasification is influenced by the speed of flow in ranges I and II. In range III, however, the speed of flow does influence the thickness of the adhering boundary layer. Here, a decrease in the boundary layer thickness results in a steeper gradient of concentration, in stronger boundary film diffusion and in a greater intensity of gasification (Fig. 5).

2. Measurements

2.1. Apparatuses

2.1.1. Gas-analytical method

For determining the reactivity of fine-grained coke we have used an apparatus (Fig. 6) which differs only slightly from that designed by Koppers and Jenkner (15-17). Recent experiments of Dahme and Junker (18) as well as of Hedden have confirmed the usefulness of this arrangement and have made it possible for conclusions to be drawn from the results with regard to the kinetics of reaction (19). The measuring method (20) may be briefly described as follows:

Analytically pure CO_2 flows at a speed of $2.5 \text{ cm}^3/\text{sec.}$ through a reaction tube 20 mm in diameter. This tube is blown from quartz, the coke sample is resting upon a frit. In our tests the weight of the coke in the tube was 2.5. or 5 g. The gas flows downstream through the layer of coke and leaves the reaction zone through the frit. Through a pipe the outgoing gas flows into the analyser, viz. an azotometer, which has been adapted to the special purpose. In many cases an infra-red analyser was used. The oven is designed in such a way that the reaction temperature is reached after 10 minutes and the first measurement can be carried out after 15 minutes. The temperature is measured 10 mm above the frit with a platinum-rhodium couple.

2.1.2. Measurements on lumps of coke

For the determination of the intensity of gasification of lumpy coke up to temperatures of 1500°C an apparatus has been developed (see Fig. 7) which is not based on the principle of gas analysis but on the gravimetric determination of the loss of weight. The samples used in this method, are coke cylinders 40 mm high and 20 mm in diameter. A ceramic tube is suspended from a balance which records the time and the loss of weight. Through the tube a platinum-rhodium couple is introduced into the coke sample. This arrangement makes it possible to continuously observe the temperature of reaction in the coke sample during

weighing. Because of the endothermic reaction, this temperature differs from the temperature of the gas; at high temperatures the difference may reach values of some 50 °C. The throughput of gas is 400 l/h for each measurement. This means that the concentration of CO in the outgoing gas is only small and negligible in the calculation.

2.2. Measuring results

Our reactivity measurements were preceded by investigations intended to determine the influence of different factors upon the measuring accuracy.

2.2.1. Material used and sampling method

The electrode graphite used in our tests was ash-free, and thanks to its high graphitizing temperature it could be looked upon as a good primary material for the measurements intended. Microscopical determination of the pore volume and the pore structure, however, revealed significant differences from which an influence upon the reactivity was to be expected. In fact, the values found varied within the following limits:

Porosity:	19.3 to 29.3 %
Average pore size:	14 to 19 μ
Number of pores per mm:	12 to 16

The electrode graphite samples were received from the producer in form of cylinders 20 mm in diameter. For the tests they were put to size, 40 mm long. The granular samples were obtained by grinding several cylinders.

Particularly careful sampling was required for the metallurgical coke which had been made in a semi-industrial coke oven at a heating flue temperature of 1300 °C; in fact, wide fluctuations in the properties of the individual pieces of coke have to be expected even if they come from the same charge. The coke was dry-quenched in an air-tight chamber; its ash content was 8.08 %. The sampling method was as follows: A representative sample was taken from about 150 kg of coke; this sample was crushed and screened into two fractions 3 - 2 mm and 1 - 0.5 mm. From the remaining coke long lumps were selected, extending from the wall of the coke oven up to its center, and well-preserved at both ends. Part of these lumps were cut into pieces so that the outer, the middle and the inner ends were separately available and could be ground and screened into the same fractions as the mean sample. From the remaining lumps cylindrical samples were prepared, by means of a 20 mm hollow drill, and these cylinders were grouped, according to their position in the big lumps. The number of utilizable cylinders was rather limited on account of the cracks and fissures in the coke.

2.2.2. Weight loss during high-temperature treatment in nitrogen.

It is well known that coke will lose weight in inert atmosphere at temperatures higher than the carbonizing temperature. It was necessary for us to determine the amount of this loss in order to estimate the weight of the error introduced into the gravimetric measurements. In

Fig. 8 the loss of weight is plotted against the time for different temperatures. Between 900 °C and 1500 °C the curves are similar. After a steep rise during the first 30 minutes they become flatter. The loss of weight reaches considerable values, e.g. 10 % at 1500 °C after 20 hours. The qualitative explanation of this phenomenon is very simple. Apart from after-carbonization at temperatures beyond the carbonization temperature, adsorbed gases are liberated, although to a lesser degree, volatile inorganic ash components are distilled, and oxides in the ash are reduced by the surrounding carbon, especially at high temperatures. A quantitative determination of these different concomitant phenomena, however, seems hardly possible.

2.2.3. Temperature difference between gas and coke

In the course of our preliminary tests we found out that the temperature of the coke which had been attained in nitrogen fell off when carbon dioxide was fed to the apparatus. This fact is due to the endothermic character of the gasification reaction which consumes more heat than the quantity supplied to the coke by radiation from the wall of the oven and, to a lesser degree, by convection. With decreasing temperature of the coke, the heat transfer is improved, and at a certain temperature difference radiation will be sufficient to make up for the heat consumed by the gasification reaction. Fig. 9 gives the results of measurements which show the difference of temperatures reigning in the ambient gas on the one side and in the core of the coke pieces on the other at different reaction temperatures.

Up to 1100 °C no perceptible difference is to be observed, as the heat required for the reaction at the given temperature is supplied by radiation. With rising temperature, however, the reaction speed increases rapidly and the heat consumption of the reaction will increase to such a degree that a considerable temperature difference does appear. Beyond 1400 °C the curve is flattening out which indicates that the reaction has reached range III where the gasification intensity becomes a function of the boundary film diffusion and is, according to equation (30), practically independent of the temperature.

2.2.4. Burn-off as a function of time

The burn-off in CO₂ as a function of time was determined on cylindrical samples, using only the gravimetric method. It was found that at the same temperature and after the same time the loss of weight of the graphite cylinders differed very much. This is to be explained by the large differences of the pore volume, as mentioned above. In range III where the internal structure of the graphite cylinders is no longer influential upon the gasification reaction, these differences disappear.

As expected, the differences of burn-off were still larger in the tests on coke cylinders. But here, as before, we could observe the trend that at high temperatures the burn-off after the same lapse of time was constant, no matter whether the samples had been taken from the middle of the chamber or from the wall of the oven. At lower temperatures it is always the samples taken from the middle of the chamber that show the highest loss of weight.

A comparison of the burn-off curves of graphite and coke leads to the result that for graphite the loss of weight per unit of time remains almost constant even after gasification of 50 % of the material. In case of coke, a slow-down of the loss of weight per unit of time with progressing combustion is clearly evident, at least up to 1200 °C. It is most of all the coke samples taken from the middle of the chamber that show this trend.

2.2.5. Reactivity of lumps between 900 and 1500 °C.

From the burn-off curves the reaction speed can be calculated using equation (9). In Fig. 10, the values calculated in this way have been marked on an Arrhenius diagram similar to that shown in the first part of this paper.

The lower curve represents the measurements made on graphite, the upper one on coke. The diagram shows the reaction speed at different stages of burn-off, ranging between 10 and 50 %. The lower section of the graphite curve, up to 1200 °C, is a straight line. From the gradient we can calculate the activation energy for the purely chemical reaction in range I; its value is 65 kcal/Mol. After a short arch the curve adopts again the form of a straight line starting at 1400 °C with a flat gradient. The activation energy in the range of pore diffusion, as calculated from the gradient of this second straight part, amounts to 34 kcal/Mol. This value agrees fairly well with the theoretical postulates according to equation (17), from which it is to be expected that the activation energy in this range should be 50 % of what it amounts to in range I. As for the conditions in the range of boundary film diffusion, the measurements made do not permit any conclusions to be drawn.

The upper curve of Fig. 10 shows the results of measurements made on coke. In the lower part the individual values found by this method are so widely dispersed that nothing can be said about the activation energy, but we come back to this question later on. It is interesting to note that this wide dispersion of the individual values disappears more and more. This proves that the chemical reactivity of the coke samples, taken from the different parts of the oven, differs very much. In fact, the lumps taken from the middle of the oven show a higher reactivity than those taken from the wall. This is to be explained by the fact that the final carbonization temperature reigned much longer near the wall of the oven which entails a higher degree of gas emission and a decrease in reactivity.

With rising temperature the wide dispersion of the values measured disappears; beyond 1350 °C all points are close together and differences caused by the position of the samples in the coke oven are no longer noticeable. The conclusion to be drawn from this observation is that with rising temperature the importance of the chemical properties decreases more and more, whereas structure and external surface become the dominating factors. This statement is confirmed by a comparison of the graphite and the coke curves which approach with rising temperature. In the pore diffusion range whose starting point for electrode graphite is about 100 °C higher than in the case of metallurgical coke, the ratio of the gasification intensities goes down to 1.6 at 1300 °C. At this temperature the internal structure of the coke becomes the decisive factor. Above 1300 °C the ratio of the gasification intensities of both materials is about 1.5 on the average, which corresponds to the difference.

of their apparent densities. It seems that the measurements were carried out not yet entirely within the limits of range III, i.e. the zone of pure boundary film diffusion.

2.2.6. Reactivity in dependency upon the position of the coke in the oven

In Fig. 11 we have reproduced the reactivity values of the fine-grained mean samples from the three zones of the oven as determined by the coincide gas-analytical method. It is understandable that the values obtained from these mean samples do not show the dispersion which was observed with the cylindrical samples. Here all the values measured coincide with the Arrhenius lines; this is true of the 3 to 2 mm as well as of the 1 to 0.5 mm size fraction. In both cases the reactivity increases from the wall of the oven towards the centre. In the preceding chapter it was already said that this is due to the final temperature of the coke, and to the length of time during which the final temperature has been effective. From the wall of the oven up to its centre line the reactivity increases by more than 100 %. The results obtained from the sample representing the whole of the charge do not agree with the mean value of the samples representing the three different zones of the coke oven. This leads to the conclusion that there is no linear relation between reactivity and the position of the coke in the oven. As the Arrhenius lines are parallel, the activation energy is the same for all measurements, irrespective of the position of the coke in the oven, namely 67 kcal/Mol.

2.2.7. Relation between reactivity and coke size

The theoretical considerations have made it clear that in the range of purely chemical reaction, i.e. range I, diffusion need not be taken into account. This is to say (Fig. 12) that the coke size does not matter, because below a certain temperature the gasifying agent (CO_2) will reach the whole reactive surface of the coke pieces, even of different diameter, without any perceptible decrease in concentration as compared with the ambient gas.

The experimental values confirm the conclusions reached on theoretical grounds. In Fig. 10 we have marked on the graphite curve the results obtained from both cylindrical samples and the granular samples 3 - 2mm. In the range of temperatures examined (1000 - 1100 °C) the values agree perfectly. For metallurgical coke Fig. 12 shows that the reactivity measured on lumps and on granular samples is the same up to 1050 °C. Above this temperature the cylindrical samples show the influence of the pore diffusion which, in the case of granular material would only appear after a further rise of temperature. These results, however, are only valid for coke originating from the chamber wall. Similar measurements on lumps from the centre of the oven led to a wider dispersion of the results so that it is not possible to draw exact conclusions from them.

In Fig. 11 we have also given the results of measurements made on granular coke of different size. Here the finer size fraction 1 - 0.5mm, does not show the same reactivity as the 3 - 2 mm fraction. This observation is no argument against the theory; it finds its explanation in the treatment after sampling. The finer fraction will always be composed

of unhomogeneous material. Crushing and grinding leads to a concentration of high-ash and weaker particles, and differences are unavoidable. Further investigations have shown that to all appearance the ash content is an important factor.

2.2.8. The influence of ash on reactivity.

In a large series of tests which are still going on, we are studying the influence of the ash content and the ash components on the reactivity of the coke. Very clean coal (ash content under 0.5 %) was coked with selected additions. It was found that Boudouard's reaction is accelerated by iron oxides and CaCO_3 , whereas SiO_2 will slightly inhibit the reaction. Very efficient is Na_2CO_3 . The following table shows the first results of reactivity tests made on very clean coke, with or without additions, at a temperature of 1050°C ; the coking temperature was 1150°C in all cases.

Material	Addition	k_m at 1050°C ($\text{cm}^3/\text{g sec}$)
Very pure coke	-	0.485
"	SiO_2	0.304
"	Fe_3O_4	0.825
"	CaCO_3	2.78
"	Na_2CO_3	7.55

For the time being we are not able to say whether the large differences between these values are due to catalytic or other influences.

Literature

- 1) Handbuch der Katalyse I, G.-M. Schwab, Wien, Springer-Verlag (1943)
- 2) Catalysis Vol. 2, Paul H. Emmett, Reinhold Publ. Co., New York (1955)
- 3) Placed to the Meeting of Experts on the Reactivity of Coke and semi-coke of the ECONOMIC COMMISSION FOR EUROPE COAL COMMITTEE (1962)
- 4) H. Echterhoff, K. G. Beck und W. Peters, Blast Furnace, Coke Oven, and Raw Materials Proceedings, Philadelphia, Vol. 20 (1961) S. 403-414.
- 5) W. Peters und H. Echterhoff, Blast Furnace, Coke Oven, and Raw Materials Proceedings, Philadelphia, Vol. 20 (1961) S. 158-170.
- 6) K. Hedden, Dissertation Göttingen (1954)
- 7) E. Wicke, K. Hedden, Z. Elektrochem. 57, 636/41 (1953)
- 8) E. Wicke, Fifth Symposium on Combustion, Univ. of Pittsburgh, 1954, Reinhold Publ. Co., New York, 1955, 245/52
- 9) K. Hedden, Brennstoff-Chem. 41, 193/224 (1960)
- 10) C. N. Hinshelwood, J. Gadsby, K. W. Sykes, Proc. Roy. Soc. (London) A 187, 129/51 (1946)
- 11) J. Gadsby u.a., Proc. Roy. Soc. (London) A 193, 357/76 (1948)
- 12) F. J. Lang, K. W. Sykes, Proc. Roy. Soc. (London) A 193, 377/99 (1948)
- 13) K. Hedden, E. Wicke, Proc. Third Conference on Carbon, Buffalo (1957)
- 14) W. Peters, G.-W. Lask, Brennstoff-Chem. 42, 84/90 (1961)
- 15) H. Koppers, A. Jenkner, Arch. Eisenhüttenw. 5, 543/547 (1931/32)
- 16) H. Koppers, A. Jenkner, Koppers-Mitt. 1, 15/16 (1922)
- 17) H. Koppers, VDI-Zeitschrift 66, 651 (1922)
- 18) A. Dahme, H. J. Junker, Brennstoff-Chem. 36, 193/224 (1955)
- 19) W. Peters, Glückauf 96, 997/1006 (1960)
- 20) W. Peters, G.-W. Lask, Brennstoff-Chem. 42, 323/328 (1961)

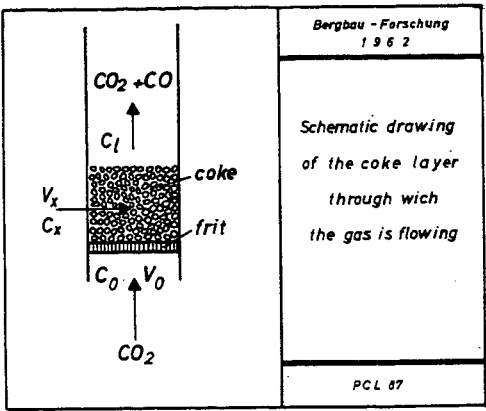


Figure 1

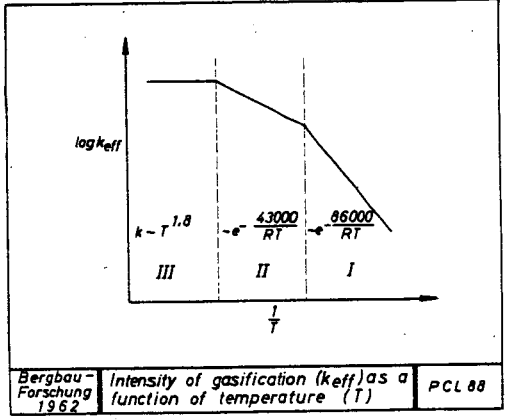


Figure 2

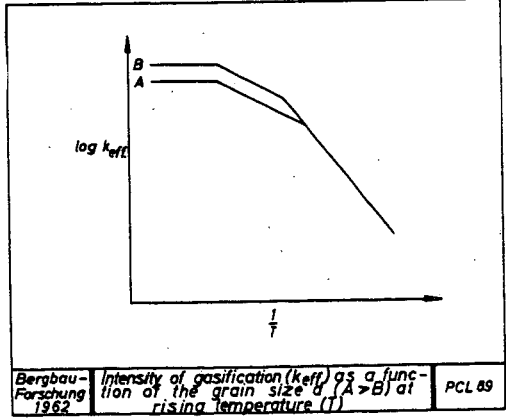


Figure 3

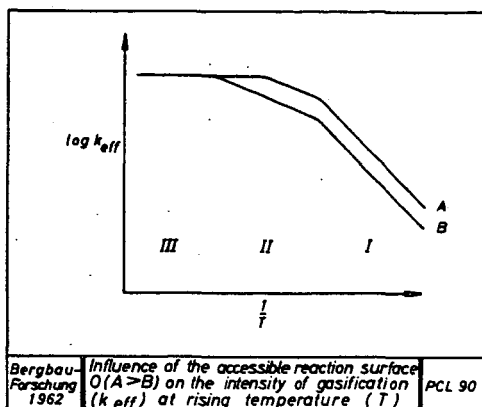


Figure 4

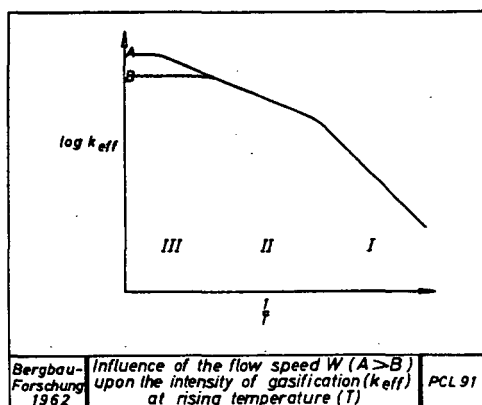


Figure 5

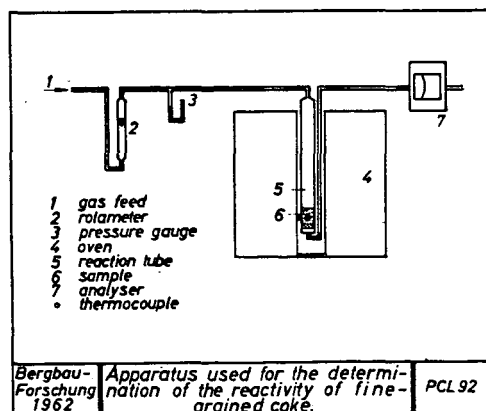


Figure 6

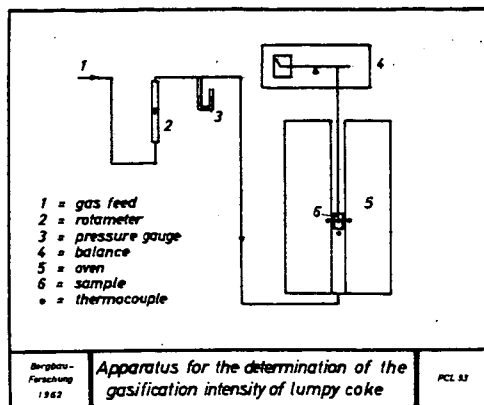


Figure 7

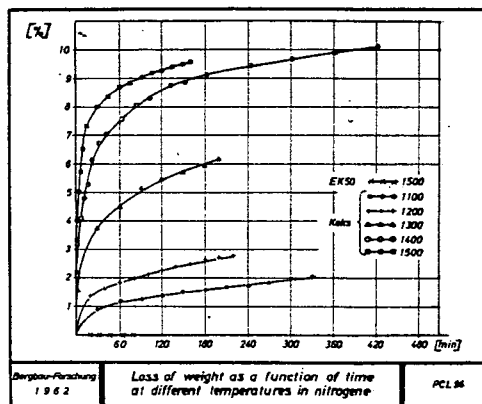


Figure 8

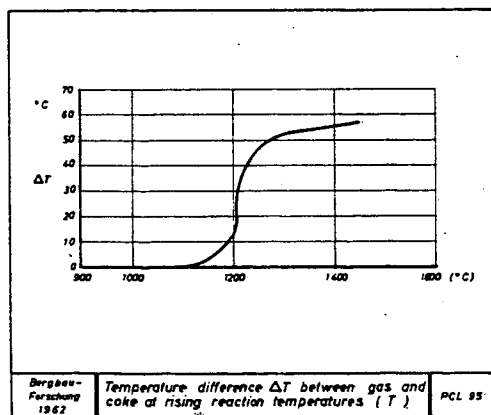


Figure 9

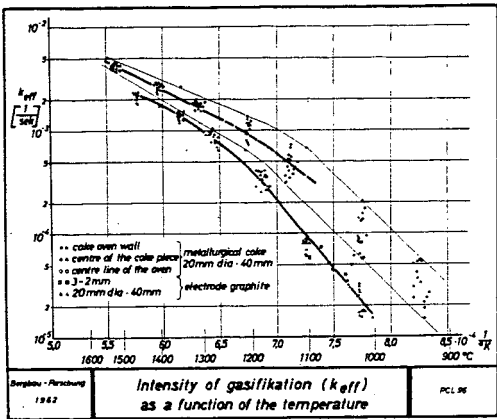


Figure 10

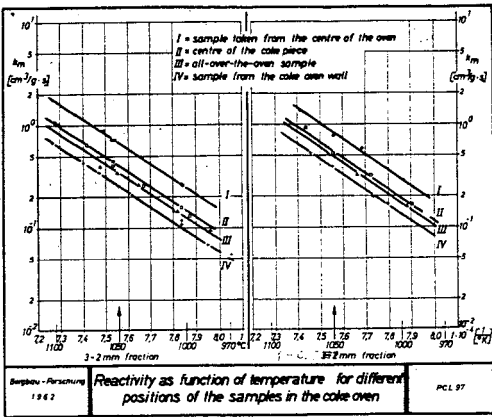


Figure 11

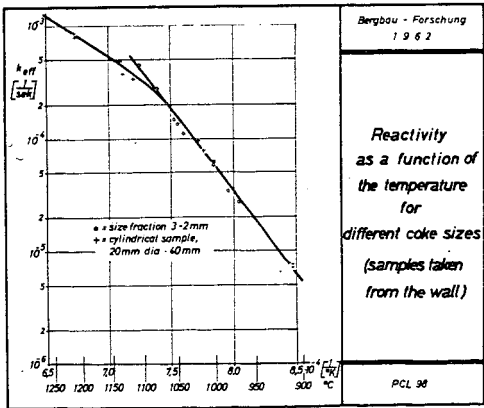


Figure 12